





YW

REPORT NO. NADC-81172-60



A POLLUTION ABATEMENT CONCEPT; EVALUATION OF ECO-TEC CHRONIC ACID RECOVERY SYSTEM

H. J. Lee
Aircraft and Crew Systems Technology Directorate
NAVAL AIR DEVELOPMENT CENTER
Warminster, Pennsylvania 18974

NAVAL AIR REWORK FACILITY

Naval Air Station

Jacksonville, Florida 32212

' 16 September 1981

PHASE REPORT
AIRTASK A340/0000/001B/6F57-572-401
Work Unit VQ301



APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLINITED

Prepared for NAVAL MATERIAL COMMAND Department of the Navy Washington, DC 20361

BIN TILE COPY

01 21 82 107

NOTICES

REPORT NUMBERING SYSTEM - The numbering of technical project reports issued by the Naval Air Development Center is arranged for specific identification purposes. Each number consists of the Center acronym, the calendar year in which the number was assigned, the sequence number of the report within the specific calendar year, and the official 2-digit correspondence code of the Command Office or the Functional Directorate responsible for the report. For example: Report No. NADC-78015-20 indicates the fifteeth Center report for the year 1978, and prepared by the Systems Directorate. The numerical codes are as follows:

CODE	OFFICE OR DIRECTORATE
00	Commander, Naval Air Development Center
01	Technical Director, Naval Air Development Center
02	Comptroller
10	Directorate Command Projects
20	Systems Directorate
30	Sensors & Avionics Technology Directorate
40	Communication & Navigation Technology Directorate
50	Software Computer Directorate
60	Aircraft & Crew Systems Technology Directorate
70	Planning Assessment Resources
80	Engineering Support Group

PRODUCT ENDORSEMENT - The discussion or instructions concerning commercial products herein do not constitute an endorsement by the Government nor do they convey or imply the license or right to use such products.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered)

	,
REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 2. GOVT ACCESSION NO.	1. RECIPIENT'S CATALOG NUMBER
NADC-81172-60 AD-A109893	
4. TITLE (and Substite)	S. TYPE OF REPORT & PERIOD COVERED
A POLLUTION ABATEMENT CONCEPT: EVALUATION OF	Phase
ECO-TEC CHROMIC ACID RECOVERY SYSTEM	
	5. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(e)	S. CONTRACT OR GRANT NUMBER(s)
H. J. Lee, NAVAIRDEVCEN, Narminster, PA	
S. O'Brien and H. M. Gundersen	•
NAVAIREWORKFAC, Jacksonville, FL	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TABK
NAVAIREMORKFAC, Jacksonville, Florida	
NAVAIRDEVCEN, Warminster, Pennsylvania	AIRTASK A340/0000/001B/6F57-
	572-401, Work Unit VQ301
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Naval Material Command	16 September 1981
Department of the Navy	13. NUMBER OF PAGES
Washington, DC 20361	19
14. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office)	18. SECURITY CLASS. (of this report)
Naval Air Development Center	Unclassified
Aircraft and Crew Systems Technology Directorate	1
Warminster, Pennsylvania 18974	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
	<u> </u>
16. DISTRIBUTION STATEMENT (of this Report)	
Approved for Public Release; Distribution Unlimit	teđ
1	- .
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, If different tre	m Report)
i	
18. SUPPLEMENTARY NOTES	
	!
	j
19. KEY WORDS (Centinue on reverse side if accessary and identify by block number)	
10. No. 1 montes (securities at termine side it mesecont) and termine of most manner.	·
Effluent Treatment, Chromic Acid Recovery, Election	roplating,
Pollution Abatement	
1	
ID. ABSTRACT (Continue on reverse side if necessary and identify by block mumber)	
The evaluation of a short bed rapid cycle ion exch	
control at the source has been completed. An ECO-	TBC short bed rapid cycle
ion exchange unit Model Cl2, was installed in a ch	romium electroplating line.
at MAVAIRSMORNTAC, Jacksonville. The unit is design	
and particulate matter from the first rinse tank at	
the second rinse. It should recover 99% of the chi	
unit. This report is a critique on work done at MA which is presented as Appendix A of this report.	MENDMONNE ME ! NECKRONATTIAL!
DD . FORM 1473 EDITION OF 1 NOV 65 IS DESCRETE	

DD , JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE 5/N 0102-LF-014-6601

UNCLASSIFIED

•		
	•	
-		
•		
	·	
· · · · · ·		
	·	
		•

UNCLASSIFIED

TABLE OF CONTENTS

																						Page No.
INTRODUCTION	•	•	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	•	•	•	•	•	2
DISCUSSION	•		•	•	•	•	•	•	•	•	•	•	•	•	•	•	•			•	•	2
OBJECTIVE						•					•	•										2
RESULTS .			•				•	•	•			•	•	•		•	•	•	•	•		2
CHEMISTRY (Œ	T	HE	I	on	E	XC.	HA.	NG	E i	PRO	OC	ES:	5	•	•	•	•	•			2
INITIAL PRO)BI	LBI	YS	•	•	•	•		•	•	•	•	٠	•	•	•	•	•	•	•	•	3
MODIFICATIO	ON:	S	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	3
SUMMARY	•	•	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	•	•	•	•	•	4
RECOMMENDATIO	ON	•	•	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	•	•	•	•	5

APPENDIX A

NAVAIREWORKFAC, Jacksonville Materials Engineering Laboratory Report 1-81 "ECO TEC Chrome Acid Recovery Unit Evaluation"

7
Incomion For
n gn182 💆
C TiB
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
:: leation
R
I proportion/
vallability Codes
At all and/or
Dist Special
1.0
14
PTIG
(COPY)
3

INTRODUCTION

The discharges of the chromium baths that the Naval Air Rework Facilities (NAVAIREWORKFACS) use to plate aircraft parts invariably and unavoidably find their way into the environment. Since these discharges, which contain toxic wastes, especially hexavalent chromium, constituted an extremely pollutive hazard, the Environmental Protection Agency (EPA) has established a zero discharge requirement commencing in 1980. To meet these stringent effluent standards, a feasibility study was initiated to determine the merits of recycling chromium plating bath constituents.

At the direction of the Naval Air Development Center (NAVAIRDEVCEN) and under Aircraft Pollution Abatement Program, AIRTASK No. A340/0000/001B/6F57-572-401, the ECO TEC Cl2 chromic acid recovery unit for plating systems was purchased and installed in the plating shop at NAVAIREWORKFAC, Jacksonville. This unit has been installed and functional for a period of one year and its evaluation has been completed.

DISCUSSION

OBJECTIVE

The primary objective of the evaluation of the ECO TEC Chrome Acid Recovery System was to determine its effective ability to purify rinse waters for rinsing chrome plated wares, recover chrome plating electrolyte for plating reuse and to reduce pollution resulting from the chrome plating operation.

RESULTS

Observation and results of this NAVAIREWORKFAC, Jacksonville evaluation are described in Appendix A.

CHEMISTRY OF THE ION EXCHANGE PROCESS

To understand the principles of the chemistry involved in the ion exchange processes of the unit, a concise outline of the chemical reactions is given on page 2 of Appendix A. Basically, cation exchange resin bed #1 is designated as Cation #1 (Pretreat), Anion exchange resin bed as Anion, Anion exchange resin regeneration as Anion Regeneration, and cation exchange resin bed #2 as Cation #2. However, the chemical reactions for the acid regeneration of the cation exchange resin beds #1 and #2 are added below:

Cation Bed #1 $ZR^{-}H^{+} + XCrO_{4} + XR_{2} + H_{2}CrO_{4}$ (Pretreat) X=Ca, Mg, Fe, Cr(III), Ni, Al, etc. R=ResinAnion Bed $2R^{+}OH^{-} + H_{2}CrO_{4} + R_{2}CrO_{4} + 2H_{2}O$ (Removes Cr(VI), returns deionized $H_{2}O$ to rinse tank)

Anion Bed Regeneration $R_2Cr0_4 + 2NaOH + 2ROH + Na_2Cr0_4$

(Removes chromate from bed)

Cation Bed #2 $2R^{-}H^{+} + Na_{2}CrO_{4} + 2RNa + H_{2}CrO_{4}$

(Regenerates chromic acid from chromates)

Acid Regeneration with H₂SO₄

Cation Bed #1 $R_2^T X + H_2 SO_4 + 2R^T H^+ + X_2 SO_4$

X = Metallic impurities

Cation Bed #2 $R^T Na^+ + H_2 SO_4 + 2R^T H^+ + Na_2 SO_4$

In principle, the original unit consists of a very short column or bed with a small resin inventory which requires rapid cycling. Because the resin has low loading, i.e., resin regeneration long before saturation, the cycle time is further reduced. The short bed allows the use of fine resins, which are less susceptible to fluid flow problems, to maximize surface area and increase exchange rates. In addition, it has the features of very little void space (more fluid-resin bed contact), uses counter current regeneration technique where density effects are used advantageously, i.e., "Flow directions are designed to keep the lighter fluid on top thus gaining a kind of "piston" effect that results in plug flow and good rinsing characteristics" and is fully automatic.

INITIAL PROBLEMS

From the beginning, NAVAIREWORKFAC, Jacksonville experienced difficulty with the operation of the original equipment because of a high frequency of breakdowns. Modification and replacement of parts (some of a different type) were required before the unit became satisfactorily operational.

Anion resin bed fouling was encountered several times due to the precipitation of heavy metals on the anion resin bed which had bled through the cation resin bed #1. Procedures in the manual for removal of the precipitate by acid wash were inadequate and subsequent changes in the procedure resulted in no dissolved metals appearing in the effluent. Although fouling of the anion resin bed and bleeding through the cation resin bed #1 occurred, no resin degradation was observed in either case.

MODIFICATIONS

Major modifications in the procedures for the regeneration of the pretreatment resin bed were required because NAVAIREWORKFAC, Jacksonville found the ECO-TEC instruction manual for the unit, in general, extremely inadequate. Subsequent close liaisons with ECO-TEC and the suggestions

advanced by NAVAIREWORKFAC, Jacksonville have now resulted in an improved quality of instructions in the total manual.

The size of the pretreatment bed was increased because the water at NAVAIREWORKFAC, Jacksonville was too hard, also, the probe and controller assembly were replaced, two valves and one master switch were added, and a consolidation of appropriate switches were made.

Originally, the ECO-TEC Cl2 unit was purchased for the treatment of rinse water in plating operations. However, since the plating workload at NAVAIREWORKFAC, Jacksonville was small with a resultant limited dragout in the rinse water, plating bath was pumped into the rinse tank to determine the maximum concentration of hexavalent chromium in the rinse water that could be treated by the ion exchange unit. The maximum concentration found was 1,000 ppm ${\rm Cr0}_3$, as described in Appendix A. In actual practice, however, both the plating bath and rinse water were cleaned at the same time, thus, instead of pumping the plating solution into the rinse tank alone, a mixing tank was used. Because of the low drag-out in the rinse water at NAVAIREWORKFAC, Jacksonville the unit was used additionally for the successful cleaning up of the plating bath. Thus, the unit was converted satisfactorily to perform a double function. However, it must be noted that the ECO-TEC Cl2 unit by design is engineered for cleaning rinse water only and any additional functions impressed upon it is outside the intent of its design. With modification as described in Appendix A and a process analysis of the total NAVAIREWORKFAC plating system, the unit can be extended to clean the plating bath simultaneously with the rinse water.

SUMMARY

Initial problems with the unit, experienced by NAVAIREWORKFAC, Jacksonville as described in Appendix A were eliminated by modifications to the unit.

From a performance standpoint, NAVAIREWORKFAC, Jacksonville found the ECO-TEC Cl2, with these modifications, generally satisfactory and that the unit well demonstrated the applicability of ion exchange techniques in a NAVAIREWORKFAC plating shop.

From the consideration of "pay-back", the low chromium plating work-load with resulting limited drag-out experienced at NAVAIREWORKFAC, Jacksonville does not justify ion exchange recovery of chromium from rinse tanks alone. This applies only to NAVAIREWORKFAC, Jacksonville and to other NAVAIREWORKFACS with similar work loads (See Appendix A, pages A-11 and A-12).

However ion exchange recovery of chromium from the plating baths and rinse tanks simultaneously in low workload procedures appears to be an economical system to use when costs of alternate methods which include cost of chemical replenishment, waste treatment, hauling and ecological intangibles, are considered.

RECOMMENDATIONS

The overall performance of the unit modified by NAVAIREMORKFAC, Jacksonville was found to be satisfactory for chromium recovery. Recommendation is therefore made to use equivalent type equipment for nickel plating operations, especially since a companion system for nickel recovery, designed with many important features of the chromic acid recovery system incorporated, presently exists on the market. The major difference lies in the use of a different ion exchange resin for the nickel recovery.

APPENDIX A

NAVAIREWORKFAC, Jacksonville
Materials Engineering Laboratory Report 1-81
"ECO TEC Chrome Acid Recovery Unit Evaluation"
of 10 February 1981

NAVAL AIR REWORK FACILITY.

NAVAL AIR STATION JACKSONVILLE. FLORIDA 32212

IN REPLY REFER TO: Code 340:SHOB Ser 401

From: Commanding Officer, Naval Air Rework Facility, NAS, Jacksonville, FL 32212

To: Commander
Naval Air Development C

Naval Air Development Center (60613) Warminster, PA 18974

Subj: Report on Eco Tec Chromic Acid Recovery System; forwarding of

Ref: (a) NAVAIRDEVCEN ltr 1847 of 9 Mar 1976

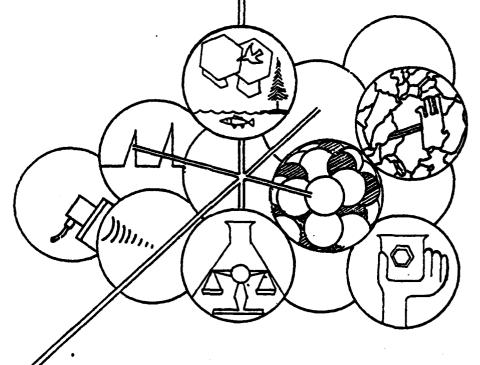
Encl: (1) Copy of NARF JAX Materials Engineering Laboratory Report No. 1-81

1. Evaluation of the subject recovery system was requested by reference (a). The system has been installed and functional for a 1-year period and an evaluation has been completed. A copy of the final report on the investigation is forwarded as enclosure (1).

H. M. GUNDERSEN By direction

Copy to: NAVAVNLOGCEN (NALC-2321)

MATERIALS ENGINEERING DIVISION



LABORATORY REPORT NO. 1-81

SUBJ: ECO TEC CHROMIC ACID RECOVERY UNIT EVALUATION

BATE: 10 FEERUARY 1981



NAVAL AIR REWORK FACILITY NAVAL AIR STATION JACKSONVILLE, FLORIDA 32212

Code 340:SHOB:bgp 10 February 1981

MATERIALS ENGINEERING LABORATORY REPORT 1-81

Subj: Eco Tec chromic acid recovery unit evaluation

Ref: (a) NAVAIRDEVCEN 1tr 1847 of 9 Mar 1976

(b) NAVAIRSYSCOM 1tr AIR-4147A:CSS of 27 May 1977

Encl: (1) Copy of form "Operating Log"

- 1. References (a) and (b) discussed and authorized the purchase of a chromic acid recovery unit for evaluation in the plating shop at NARF JAX. The unit, Eco Tec Model C12, manufactured by WIX, Incorporated, has been installed and has been functional for a 1-year period.
- Background: The need for an economically feasible method for the recovery of chromic acid from hard industrial chromium plating processes, rinses, and wastes is universal in the industry. Not only is the United States chromium supply imported from Russia and South Africa, but chromium salts are toxic to marine/ biological life and so are limited to less than . 5 part per million (p.p.m.) in outfalls from industrial water treatment plants. classical method of removal from effluent streams is by the expensive sulfite reduction/hydroxide precipitation method. procedure yields a product which is difficult to dispose of since its limited range of insolubility prohibits placing it on a landfill; it must be placed in a hazardous chemical dump. Sulfite destruction has been used locally in a continuous flow plant and has proved to be costly, not only from the man-hours required for operation, but from the excessive cost of equipment maintenance in the highly corrosive environment. Chromium from other sources in NARF; i.e., paint stripping/conversion coating has been handled by the Naval Air Station waste water treatment plant which is designed to treat two-thirds industrial waste and one-third domestic. The aerobic biological mechanism of this treatment method has been effective to date in removing pollutants, including heavy metals, in all but those instances where surges were received from spills or heavy workload. The chromium appears in the treatment plant sludge and again presents a disposal problem. Removal of chromium from the effluent stream for reuse, not treatment for ultimate disposal, is the most feasible procedure.
- 3. Equipment: The Eco Tec C12 uses conventional ion exchange techniques. Improvements in resin chemistry have overcome problems caused by chromic acid oxidation degradation. Previous resins required excessive dilution of solutions to avoid attack and other exchange inefficiencies. The C12 uses two strong acid cation resin beds and one strong base saion bed.

Subj: Eco Tec chromic acid recovery unit evaluation

Briefly the unit operates as follows:

Cation #1 $2R^{T}H^{+} + XCrO_{4} \longrightarrow XR_{2} + H_{2}CrO_{4}$

(Pretreat) X=Ca, Mg, Fe, Cr(III), Ni, Al, etc.

Anion $2R^+OH^- + H_2CrO_4 - R_2CrO_4 + 2H_2O$

(Removes Cr(VI), returns deionized H₂O to rinse tank)

Anion Regeneration

 $R_2CrO_4 + 2NaOH \longrightarrow 2ROH + Na_2CrO_4$

(Removes chromates from bed)

Cation = 2 2R H + Na₂CrO₄ - 2RNa + H₂CrO₄

(Regenerates chromic acid from chromates)

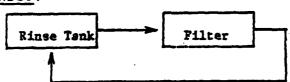
Efficiency of resin usage and saving in unit size are realized by the use of fast cycle, reciprocating flow. This procedure takes advantage of high initial rate of exchange of the resin in a low volume dead space, short bed system. By using a short cycle, the resin has a low load. All of these features allow the resin to be finer to maximize surface area and to minimize bed flow disturbances.

- a. Equipment Installation: The Cl2 is modular and can be located in an area 4-1/2' X 6-1/2' X 6' high. The rinse tank treated in this evaluation is 670 gallons, is located in the plating area, and is used to rinse parts from two hard chromium plating tanks. It was not possible to locate the Cl2 closer than 70 feet from the rinse tank so it was necessary to install an additional lift pump at the rinse tank. The following connections were made:
 - (1) 'Air (0.25 c.f.m.) filtered at 50 p.s.i.
 - (2) Water at 30 p.s.i., approximately 200 p.p.m. hardness as CaCO₃
 - (3) Electricity, 460 V 3-phase, 60 cycle, 5 amperes.
 - (4) Regenerants, concentrated sulfuric acid and 50 percent (w/v) sodium hydroxide.
 - (5) Reclaimed chromic acid storage tank.

Subj: Eco Tec chromic acid recovery unit evaluation

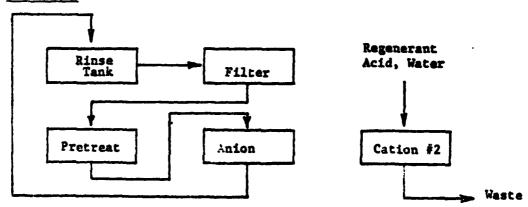
- (6) A metering pump and mixing tank were used in conjunction with the rinse tank to provide a continuous, maximum chromic acid concentration to the unit by feeding plating solution to the mixing tank when Cr(VI) levels were low in the rinse tank. In this case, the mixing tank and production rinse tank simulated the two stages of a cascade rinse. A conductivity probe and a level control sensor were mounted in this mixing tank.
- b. Operation: After manual startup, the equipment is automatically started/stopped by a conductivity cell in the rinse tank (which senses the chromic acid concentration). Various functions in the operating cycle are then controlled by adjustable timers which direct the operation of pneumatic and electrical solenoid valves to control the flows. Monitors can shut down the unit if they detect interruptions in air, water, and electrical services, or filter plugging. The unit repeats the approximately 30-minute long cycles, as long as the conductivity cell demands. It is shut down by manually activating a circuit which requires completion of the current cycle before deactivation. The cycle has three major functional sections; sketches of flows are shown below:

STANDBY:



Rinse water is pumped through the system bypassing resin beds until chromium concentration is sufficient to start a cycle.

ONSTREAM:

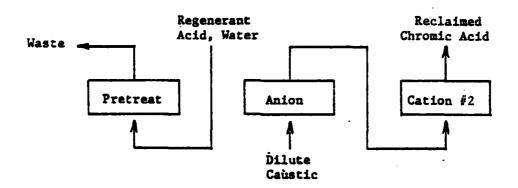


Water in beds is purified by recirculation. Cr(VI) containing rinse water is pumped through the pretreat bed, to remove metallic

Subj: Eco Tec chromic acid recovery unit evaluation

impurities, to the anion bed where the Cr(VI) is removed. Purified water is returned to the rinse tank. During this operation, the #2 cation bed is regenerated.

c. Recovery:



The anion bed is purged of Cr(VI) by dilute caustic as it is forced by air pressure from a dilution reservoir through the bed. This sedium chromate solution is then treated in the #2 cation bed and converted to chromic acid. This purge is controlled by a lower level switch in the caustic reservoir. Once activated, the flow reverses and water pushes the caustic back through the cation and anion beds into the reservoir until the upper level switch is activated. This ends the cycle. During this sequence, the pretreat bed is regenerated with acid after the void of water is returned to the rinse tank. It is washed with water until the end of the cycle.

- 4. Testing: During the testing period, 1,456 cycles of operation were completed on the C12 to check the machine function, collect test data and and perform unit maintenance. Data was collected on a form, enclosure (1). Testing was directed towards determining the amount of chromium which would require treatment, the efficiency and quality of treatment, and general performance of the equipment. Test results are summarized as follows:
- a. Drag-out. The rinse tank was monitored during normal production rinsing to quantify the chromium increase in the rinse water. Twelve different work/rack configurations showed drag-out of 2.5 4.5 gm.Cr(VI) per square foot of work surface area. The average drag-out was 3.1 gm. Cr(VI)/sq. foot. During a 3-month interval, a daily average accumulation in the rinse tank was 22.5 gm.

MELR NO. 1-81 Code 340:SHOB:bgp 10 Tebruary 1981

Subj: Eco Tec chromium acid recovery unit evaluation

- b. Maximum concentration of Cr(VI) which could be treated with cycle time intervals "as-delivered" was determined by gradually increasing the concentration in the rinse tank until bleed-through into the purified water return was excessive. It was found that the maximum concentration at which the rinse tank could operate was 1,000 p.p.m. CrO₃ in order to maintain a maximum 20 p.p.m. CrO₃ on the return. The CrO₃ in the purified return increased proportional to the CrO₃ in the rinse tank, reaching 320 p.p.m. at 3,000 p.p.m. in the rinse. The 1,000 p.p.m. CrO₃ in the feed optimized the bed loading and ultimate cycle efficiency.
- c. The C12 unit was repeatedly cycled with 1,000 CrO₃ in the rinse water. Summary of tests conducted are:

	Range of conc. of CrO ₃	рН	Hardness (p.p.m. CaCO ₃
Plating solution .	32-28 oz./gal.	• • •	
Mixed rinse water	750-1,000 p.p.m.		
Recovered CrO ₃ *	7-11 oz./gal.	<1 ∶	
Purified water**	0-20 p.p.m.	6-9	10-40
Rinse tank (2nd stage)	5-40 p.p.m.	6.5-7.5	75-100

- * Average volume recovered CrO, was 5.25 liter/cycle ** Average volume purified water was 17 gal./cycle
- d. Tests conducted which measured the quantities of CrO₃ treated and recovered per cycle agreed quite closely at approximately 350 gm. CrO₃ cycle.
- e. The recovered chromic acid was satisfactory for use as replenishment for evaporative water loss and chromic acid drag-out. The solution was free of water salts and the metallic contaminants (mixed metallic oxides of Fe(III), Cr(III), Al, Cu, Ni were found to be 0.88% in the plating solution). The reclaimed solution contained an average of .7 oz./gal. SO₄; this was removed with barium carbonate before returning it to the plating tank.

Subj: Eco Tec chromium acid recovery unit evaluation

f. Approximately 48 gallons of tap water were used for each cycle. The waste water was found to contain the following approximate concentrations of contaminants per cycle:

Total	dissolved	solids	15,000.0	mg./1
Cr			70.0	mg./1
Ni			0.5	mg./1
Cu				mg./1
Fe		•		mg./1
A1				mg.l
pН				•••

g. Regenerating chemicals used per cycle are:

Sulfuric acid (1.84 sp. gr.) 900 ml. Sodium hydroxide (50% w/v) 650 ml.

h. Cost of operation estimates were established as follows:

Regeneration Chemicals/Utilities	<pre>\$/Cycle</pre>
Sulfuric acid (1.84 sp. gr.)	.713
Sodium hydroxide	.208
Electricity	.041
Water	.019
Sewage	.031
Total	1.021

Maintenance cost estimated at 20% unit price	\$4,000
Estimated total annual operating cost for 5,000 cycles	
Cost of chromic acid for 1,700 gallon of plating bath	\$4,900
Cost of contractor hauling of sulfite treatment sludge	
from destruction of 3,900 pounds chromic acid	\$1,900

- 5. Comments and discussion on unit performance:
- a. The unit start/stop is controlled by conductivity. The probe/controller supplied with the unit proved to be the most deficient part of the system causing excessive maintenance and downtime. The probe was extremely delicate and easily contaminated. The controller range was improper for operation of the unit at chromium concentrations specified by the manufacturer; i.e., it was necessary to set the controller at the extreme lower end of the range. Spasmodic periods of unit operation with either no cycling or continuous cycling were experienced. After the probe was replaced twice, it was decided to replace the controller assembly and probe with a modified Beckman rinse tank controller which was onhand. After this change, no more problems were experienced in this area of operation.

Subj: Eco Tec chromium acid recovery unit evaluation

- b. The operating manual supplied with the unit was not adequate. It omitted important details of operation and was sketchy in general overall presentation of design considerations. This caused significant problems with the unit start-up and the familiarization of operating/engineering personnel. The manufacturer accomplished the initial start-up and training and provided service calls. However, the lack of detailed written information for this complex equipment caused excessive expenditures of time for self-education to allow handling of day-to-day problems. Probe and other electrical/mechanical malfunctions occurred with a frequency which made the operating manual deficiencies quite evident when troubleshooting was attempted.
- Anion bed fouling occurred several times during the evaluation period. This event is evidenced by chromium bleedthrough into the purified return water and by reduced concentration of recovered chromic acid. The cause is the bleeding of heavy metals through the pretreat cation bed with their subsequent precipitation on the anion bed. Removal of this precipitate requires a vigorous acid treatment. A procedure in the operating manual for anion bed acid wash was not adequate and was changed to require longer dwell time and the repetition of acid treatments until no dissolved metals appear in the effluent (colorless). Correction of this problem would require increasing the size of the pretreat cation bed to accommodate the quantities of ions encountered in the particular treatment system. An improvement is also required in the procedure for regeneration of the pretreat bed to insure that each treatment is effective. Cversizing the pretreat bed would be cost effective in the long run since it would prevent gradual degradation of the anion bed capacity.
- d. Acid and caustic regeneration and washing of the anion bed requires the full attention of an operator throughout a complex sequence which involves reversing airlines on two pneumatic valves, opening and closing three ball valves, and the manipulation of five switches. This procedure is time-consuming and requires a skilled operator. If regeneration of the bed is to be required frequently due to varied operating conditions which cannot be accommodated by an increased quantity of pretreat resin, the regeneration process should be made automatic or semiautomatic. In any event, a simple addition of two valves and a consolidation of appropriate switches to a master would make an infrequently performed operation simpler and less prone to error. Further, it was found that reversing the airlines had a tendency to loosen ferrules on the plastic connecting lines causing them to disconnect with resultant unit malfunction.

Subj: Eco Tec chromium acid recovery unit evaluation

- Presently, each process in the cycle is preset to a specific time with no flexibility or sensibility options to adjust conditions for variations in concentrations of chromic acid or other chemicals. A cycle is made consisting of certain dwell times of the influent on cation and anion beds, addition of regeneration chemicals, bed washing, and chromic acid and purified water recovery. Efficiency of operation of the unit and savings in chemicals and water would certainly result from optimization of the various functions in each cycle. This could be accomplished without unrealistic increase in equipment cost by the additions of (1) conductivity and pH sensors in the system to regulate bed washing times and ion/resin adsorption times and (2) microprocessor electronics to replace the mechanical timer. An improved timer and regulator system would allow simple adjustments by an operator when production plating operations dictate a change in rinse water quality or when the unit is to be used for plating bath purification.
- f. Regeneration chemicals are added by gravity feed from elevated polyolefin tanks which are filled by pumping from acid carboys and a caustic makeup tank. This procedure needs modification. Handling of concentrated sulfuric acid and caustic solutions in this manner is not only hazardous but is time-comsuming since an operator must be onhand during the entire operation. The solutions should be either added at ground level by chemical feed pumps or the elevated tanks must be increased to a size which requires infrequent filling. In this case, tanks/transfer pumps and lines must be totally enclosed to eliminate risks associated with such transfer and storage.
- g. The electrically operated solenoid used for acid dispensing malfunctioned twice during the evaluation period and was replaced. Additionally, the acid fill meter cannot be read without bypassing a splash shield. An improved valve and meter should be employed.
- h. Approximately 700 pounds of chromic acid were treated during the evaluation and none of the resins showed noticeable signs of deterioration.
- 6. Conclusions: The Eco Tec Cl2 generally performed satisfactorily. Other than the problems discussed in paragraph 5 above, design, construction, dependability and maintainability were adequate. The unit demonstrated well the possibilities of the use of ion exchange techniques in a NARF plating shop. It was found on a "pay-back" basis that the limited drag-out experienced with industrial hard chromium plating procedures would not justify ion exchange recovery of chromium acid from rinse tanks. The Cl2 in its present configuration requires an operator to visually inspect the various operating variables at least once per working

Subj: Eco Tec chromium acid recovery unit evaluation

shift whether the unit is operating at capacity or not. Also, normal maintenance requirements exist whether the unit is in high frequency use or not. Justification can be seen for its operation, however, for recycling baths to remove those metallic contaminants which have required disposal of baths in the past. The \$9,000 annual unit operating cost is almost offset by the cost of chemicals and contractors waste hauling (see paragraph 4h above). When the cost of chromic acid sulfite reduction treatment (cost Rot available) is added, a real savings will be realized. This saving does not include tangible and intangible benefits to the environment. Further, a recovery method is desirable since it provides a viable alternate to hauling the treated or untreated plating bath waste to hazardous waste disposal sites which are becomming more scarce and controversial. Cost estimates developed during the evaluation of this unit should allow the comparison of the ion exchange techniques to those of reverse osmosis, evaporative recovery,

7. Recommendations: Where this unit may be most effectively and economically employed in a hard chromium plating or chromic acid anodizing application is for the triple role of chromium removal from rinse water, bath decontamination, and maintenance of deionized rinse water. A simpler decationizing unit for bath purification could be used without anion/cation chromic acid recovery resin beds. Although somewhat easier to operate, this unit would be subject to the same major costs of operation as the three-bed unit; i.e., maintenance and the requirement for bath dilution prior to treatment. The size of the C12 is adequate to maintain at least two 900-gallon baths and associated rinse tanks. Dependent upon the degree and rate of bath contamination, one or two more could be handled by an increase in the bed sizes. The unit must be modified to correct the problems noted in paragraph 5 above. A 2 or 3 stage cascade rinse tank is required. The cycle set point should start the unit at 1,000 or 2,000 p.p.m.CrO3. A chemical feed pump will then be employed to keep the first stage rinse tank up to this concentration, when parts are not being rinsed, by adding contaminated plating bath. Using this technique will eliminate the need for sensors to support "on demand" recovery and regeneration sequences since unvarying influent will allow set, repetitive cycle times, optimized at the time of unit start up. The optimization should also reduce the amount of chromium from bed washing which appears in the waste effluent.

8. Acknowledgements: The assistance provided to the project by plant engineer E. Small and treatment plant operators H. Ellis and J. Maxwell is gratefully acknowledged. Their technical expertise and persistant effort contributed greatly to the success of this evaluation.

INVESTIGATED AND REPORTED BY:

Seret ÖBrien SARAH O'BRIEN

Chemical Engineering

H. M. GUNDERSEN

9/11 Sunderse

Materials Engineering Director

OPERATING LOG - ECO-TEC CHROMIC ACID RECOVERY UNIT

DATE:

	0800	1300	1800
1. Cycle number - observe counter inside electrical panel			
2. Recirculation clarity - observe 1FM when "recirculation" (8SOL) light is on		1	
3. Onstream flow rate (gpm) - observe at 1FM when "purified return" (1150L) light is on			
4. Purified Return Quality - observe ISG when "purified reutrn" (10SOL) light is on			
5. Acid Injection - observe acid meter sight tube when "cation regeneration" (16SOL) light is on			,
6. Onstream Pretreater Pressure - observe 1GG when "purified return" (11SOL) light is on	-	†	
"purified return" (11SOL) light is on			
3. Offstream Time - Take time of off-stream sequence			1
Acid Resevoir Volume - Read from tape		1	
0. Caustic Resevoir Volume - Read from tapa		 	
11. 5-Gallon Jug Volume (liters)		 	
il. Plating Tank Sample Cro3oz/gal			+
• Rinse Tank Sample Cr. פרים			+
pil Hardness, ppm as CaCO ₃			
14. Mixing Tank Sample Cro3 ppm pH			1
Hardness, ppm as CaCO ₃			
15. Purified Return Cr. ppm pH Hardness, ppm as Caω ₃			
16. Product (Reovered Cr03) Cr03.oz./gal Encounter()			+
pH A-14	•		